THE COSMOCHEMISTRY OF PROTOSTELLAR MATTER

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ABSTRACT

The different processes that can affect the chemical composition of matter as it evolves from quiescent molecular clouds into protostellar regions is discussed. Millimeter observations of molecules at high angular resolution in cold, dark clouds such as TMC–1 and L134N reveal large chemical gradients on scales of a few tenths of a pc, which are not well understood. Further, the abundances of the dominant oxygen– (H_2O, O_2, O), and nitrogen–bearing (N_2, N) species are ill determined, both observationally and theoretically, and little is known about some important carbon–bearing molecules such as CH_4, CO_2 and C_2H_2. Observations of the distribution of molecular material in disks surrounding newly–formed low–mass stars such as IRAS 16293 –2422 are just starting to become available, and reveal a complex chemistry on scales of 500–10,000 AU. Remarkable similarities are found with the chemistry observed in the high–mass star forming region Orion/KL, despite a factor of 1000 difference in stellar luminosity. A brief comparison with the chemical composition comets is made.

Keywords: Interstellar molecules, star formation, comets

1. INTRODUCTION

It is well established that stars form in molecular clouds, yet the chemical evolution that occurs during the star formation process is still poorly understood. The major questions are the extent to which the initial chemical state of the molecular cloud is retained during this process, and, conversely, how the chemical composition affects the star formation process itself. The latter point can be illustrated by noting that e.g. the efficiency of star formation depends sensitively on the fractional ionization of the cloud, which, in turn, is controlled by the extent to which ultraviolet photons and cosmic rays can penetrate the clouds. As to the first question: several processes can be identified that can potentially change the chemical state during star formation. For example, the high temperature induced by radiation from newly–formed stars can evaporate volatile grain mantles, and can open up gas–phase reaction channels that do not occur at the low temperatures normally encountered in clouds. Powerful shocks associated with stellar outflows can return refractory matter to the gas phase. Once interstellar matter enters a protostellar nebula, it can be physically and chemically modified in several more ways. Especially in the inner part of the nebula, the temperatures are high enough that nearly complete reprocessing of grains and molecules takes place; however, the amount of radial mixing between the inner and outer parts of the nebula may be limited. The chemical composition of objects in our own solar system such as comets may provide important information in this respect.

We summarize here briefly our current knowledge of the chemical state of each of the phases of the star–formation process, mostly from an observational point of view. This paper is a highly abbreviated version of a review chapter that will appear in *Protostars and Planets III* (Ref. 1), to which the reader is referred for more details.

2. INTERSTELLAR CHEMISTRY

2.1 Gas phase

The availability of a new generation of large aperture telescopes, combined with significant increases in receiver sensitivities, have resulted in the detection of more than 80 different interstellar molecules (Refs. 2, 3). Inspection of the derived abundances indicates that the chemical composition of interstellar clouds is clearly far from thermodynamic equilibrium. This is evidenced e.g. by the highly unsaturated nature of the organic molecules and the presence of molecular ions such as HCO^+. Other features that attest to a kinetically controlled chemistry include the detection of many long carbon–chain molecules (e.g. $HC_{11}N$, C_6H, C_3S, C_5O) and the high abundances of deuterated species. However, it is important to realize several serious limitations to the data. First, only molecules with a permanent dipole moment can be detected by their rotational emission lines at (sub)millimeter wavelengths, but symmetric molecules such as H_2, CH_4, C_2H_2 and N_2 cannot be observed in this way. Some of them can be searched for through their vibration–rotation absorption lines at infrared wavelengths against embedded or background infrared sources, but such studies are limited to specific lines of sight. Second, the Earth's atmosphere prevents the detection of the principal lines of molecules like H_2O, O_2 and CO_2. Thus, information on some of the principal carbon–, oxygen– and nitrogen–bearing molecules is lacking for most clouds. Third, most of the 80 molecules have been detected in only two or three well–studied sources: Orion, Sgr B2 and TMC–1, and the extent to which these regions are representative of other molecular clouds is not clear. Significant chemical variations are observed already between these three regions.

2.2 Solid phase

In recent years, the presence of icy mantles surrounding the refractory grain cores has been well established through infrared spectroscopy. Many absorption bands with widths characteristic of solid material are seen in the spectra of embedded infrared sources (Refs. 4–6). However, most of these features are still unidentified; only for the molecules H_2O, CO, CH_3OH (Ref. 7) and CO_2 (Ref. 8) is the assignment secure. Much more basic laboratory spectroscopy of icy mixtures is needed to identify the remaining features.

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2.3 Models

Many different models consisting mainly of gas-phase ion-molecule reactions have been developed to explain the observed molecular abundances in interstellar clouds (Refs. 9–11). Their success has been mixed: whereas the steady-state models can reproduce the observed abundances of simple molecules like OH, CO and CS fairly well, they fail to produce enough complex molecules like C_3H_2, C_4H and HC_3N by several orders of magnitude. They also result in too little NH_3 and too much O_2 and H_2O compared with the measured values or upper limits. Some of these discrepancies can be removed if it is assumed that the chemistry has not yet reached steady-state, so that not all carbon has been converted into CO. This leads to greatly enhanced abundances of complex hydrocarbons at early times, $t < 10^6$ yrs, because the atomic carbon can easily be inserted into the chains to build longer ones. The timescales for reaching chemical equilibrium vary from 10^6 yrs (carbon- and oxygen-bearing molecules) to 10^7 yrs (nitrogen-bearing molecules), and are comparable to the expected lifetimes of the clouds.

All models suffer from a lack of accurate laboratory or theoretical data on reaction rates at low temperatures. Different assumptions about one or two key reactions can sometimes result in predicted abundances that differ by orders of magnitude. Even for the simplest oxygen-bearing molecules, the models do not agree on which species is dominant: the models of Ref. 10 predict O_2:O:H_2O=1 : 0.46 : 0.04, whereas the models of Ref. 13 give O_2:O:H_2O=0.25 : 1 : 0.20. Care should therefore be taken in quoting model results, especially for some of the older ones which use outdated reaction sets.

Recent developments in modeling include efforts to describe the clumpy structure of molecular clouds (Ref. 12); calculations of cosmic-ray induced photodissociation processes inside dense clouds (Ref. 13); studies of the influence of large molecules such as PAHs (Refs. 14, 15); considerations of the depth-dependent structure of clouds located close to young, hot stars (Refs. 16, 17); and treatments of evolutionary processes (Refs. 18, 19). In addition, several models have attempted to include grain-surface processes (Refs. 20–22, 6). Two different scenarios can be distinguished: those in which the grains are only passive sinks of molecules, and those in which catalytic reactions actively produce new molecules. A major unsolved problem is how these molecules can be efficiently returned to the gas phase.

3. CHEMICAL STATE OF QUIESCENT (?) CLOUDS

In order to study the effects of star formation on the chemistry, it is necessary to delineate the chemical state of dense clouds prior to star formation. Since the models are not yet reliable enough in this respect, it is important to have accurate information from observations. Two regions in which currently no star formation is thought to occur have been studied in great detail: TMC-1 and L134N.

The TMC-1 core is a small elongated dense ridge of approximate dimensions 0.6×0.06 pc in the Taurus clouds with a total mass less than 40 $M_\odot$. Figure 1 shows the distribution of the NH_3 and HC_7N molecules along the TMC-1 ridge at about 40″ resolution, corresponding to 0.03 pc at the adopted distance of 140 pc (Ref. 23). The (0,0) position is the peak in the cyanopolyyne emission at which many other complex molecules have been observed. It is apparent that significant differences occur in the distributions of the two molecules. Such differences can be due either to variations in the excitation conditions along the ridge or to true chemical abundance variations. The former possibility has been carefully considered, but was found to be small compared with the latter one: the HC_7N/NH_3 abundance ratio varies genuinely by more than an order of magnitude over the scale of a few tenths of a parsec.

Similar abundance variations on small scales have been found in the L134N cloud (Ref. 24). Here the NH_3 and HCO^+ distributions differ significantly from that of e.g. CO and CS, whereas the SO emission peaks at yet another position. Long carbon chain molecules are clearly less abundant in this cloud than in the southern part of TMC-1, but the SO and SO_2

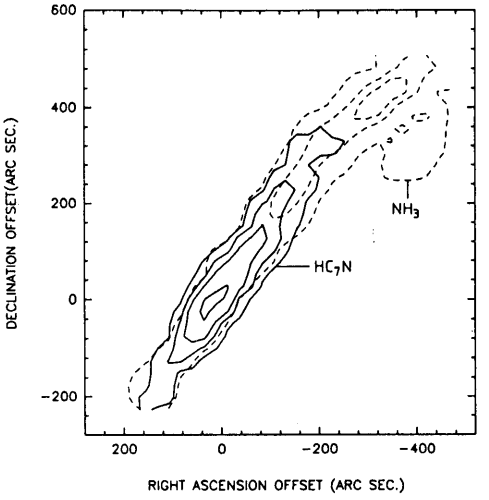

Figure 1. *Column density distribution of HC_7N (full lines) in TMC-1 compared with that of NH_3 (dashed lines). Possible gradients in excitation temperature across the TMC-1 ridge have been neglected in making these maps (from Ref. 23).*

abundances are at least an order of magnitude higher. The chemistry in L134N resembles more that found in the northern TMC-1 clump than in the southern one.

What causes the striking chemical differences between the northern and southern peaks in TMC-1, and between TMC-1 and L134N? Most chemical models have focussed on explaining the abundances in the southern part, but have succeeded only in a time-dependent calculation at an early age of a few times 10^5 yrs. In order to explain the abundance variations along the ridge, the northern part would have to be significantly older. However, there is little observational evidence to support this statement. Variations in density along the ridge could result in different timescales for depletion of the molecules, but detailed modeling of this scenario has not yet been performed. The lack of complex carbon-chain molecules in L134N is consistent with its estimated age of at least 10^6 yrs. However, the small scale variations in this cloud are not easily accounted for, although it has been suggested that variations in the elemental gas-phase O/S ratio could play a role (Ref. 24).

One possible explanation, which has not yet been discussed in the literature, is that even in TMC-1 and L134N, star formation may already be taking place and influencing the chemistry. If cold, low-luminosity protostars in a very early stage of evolution were present, they would not show up as strong *IRAS* point sources, but may still affect the chemistry if they were already in the outflow phase. In fact, a low-luminosity *IRAS* source with associated high-velocity CO outflow emission has been detected only 2′ west of the northern TMC-1 NH_3 peak (Ref. 25), and very recently, a 1 millimeter continuum source has been found at the NH_3 peak in L134N (Ref. 26). Although the latter observation does not necessarily imply the presence of a protostar, it is consistent with the general correlation between NH_3 cores and star formation which has been found in Ref. 27. It suggests that regions in which NH_3 is abundant indeed represent a later stage in the chemical evolution than those in which long carbon-chain molecules are abundant.

In summary, the question "what is the chemical composition of a dark cloud prior to star formation" cannot be answered in detail at present. It may be a challenge to find a dark cloud which is truly quiescent and in which star formation is definitely not yet occurring and affecting the chemistry. It should also be noted that in neither TMC-1 nor L134N have the *dominant* oxygen- and nitrogen-bearing molecules H_2O, O_2, O, N_2 or N been observed directly. Only for N_2 have indirect clues about its abundance been obtained from measurements of the related N_2H^+ ion.

4. CHEMICAL STATE OF STAR-FORMING REGIONS

Recent surveys at (sub)millimeter and infrared wavelengths (e.g. Refs. 28, 29) have resulted in the identification of at least 40 compact dust regions associated with young stellar objects. This list contains sources which span stellar luminosities from 10 to 10^5 $L_\odot$ and a range in obscuration from visible stars to objects so deeply embedded that no 2 μm source is detected. Estimates of the masses of circumstellar material range widely from less than 0.1 to 10 $M_\odot$ or more.

As two of the nearest and brightest star forming molecular clouds, the core of the Orion nebula and the IRAS 16293 −2422 core in the ρ Ophiuchi cloud present unique opportunities to examine the complexity and evolution of interstellar chemistry in two very dissimilar environments, i.e., high- versus low-mass star formation. We present here an overview of the results gleaned from high resolution millimeter and submillimeter spectral line surveys of these regions along with aperture synthesis maps of molecular emission. Emphasis will be placed on the alteration of the chemical composition of the parent molecular cloud by the star formation process.

4.1 Low-mass star formation: IRAS 16293 −2422

IRAS 16293 −2422 is a young far-infrared object of 27 $L_\odot$ located in the nearby Ophiuchus cloud complex. It was originally identified as a possible protostar with a molecular outflow (Refs. 30, 31) and was suggested to have a spherically symmetric infall (Ref. 30). While the claim for infall is still controversial, the central object associated with the far-infrared emission is a rich source of molecular line and long-wavelength dust emission. Dust continuum emission from IRAS 16293 −2422 has been observed at a wide range of wavelengths with the most revealing data being recent interferometer maps at 4″.3×2″.4 resolution at λ=2.7 mm (see Fig. 2d), which resolve the region into two components separated by 830 AU (5″.2) along a NW-SE axis (Ref. 32). The majority of the dust in the system is contained in these two components which are coincident with weak centimeter emission from ionized gas (Ref. 33). The overall spectral energy distribution is well fitted by a 40 K blackbody with a λ^{-1} to λ^{-2} emissivity law.

Interferometer maps of IRAS 16293 −2422 have also been made for several molecules. The $C^{18}O$ J=1→0 emission, presented in Fig. 2a at 4″×6″ resolution, is coextensive with the dust emission, and shows a velocity shift of 2.4 km s^{-1} from NW to SE consistent with orbital motion. Assuming point masses, the mass of the system is around 1.5/sin i $M_\odot$, where i, the orbital inclination, is approximately 90° (Ref. 34). The CS J=2→1 emission reveals a similar structure (Ref. 35). On the other hand, the NH_3 emission, shown in Fig. 2b, arises from a larger region (8000 AU diameter) with a kinetic temperature of 15–20 K (Ref. 34). Yet a different distribution is seen for the SO molecule, as Fig. 2c at 4″.2×2″.4 resolution demonstrates: very strong SO 2_3–1_2 emission is seen from the SE component, but no detectable emission comes from the other component. Finally, the HCO^+ 1–0 emission appears more associated with the outflow, being extended considerably NE–SW (Ref. 36). Thus, at 500–800 AU resolution, the various molecular species exhibit significantly different spatial distributions.

IRAS 16293 −2422 therefore appears to be a very young binary system in which both components are still surrounded by significant amounts of gas and dust. The SE source is the more active of the two with double lobed centimeter radio emission, strong SO emission, as well as H_2O masers tracing its outflow activity (Ref. 37). The NH_3 emission appears to be distributed in a ring with radius 3000 to 4000 AU surrounding the central sources. The dearth of ammonia emission from the central components is likely to be due to an actual decrease in NH_3 abundance. A model of the region is presented in Fig. 3.

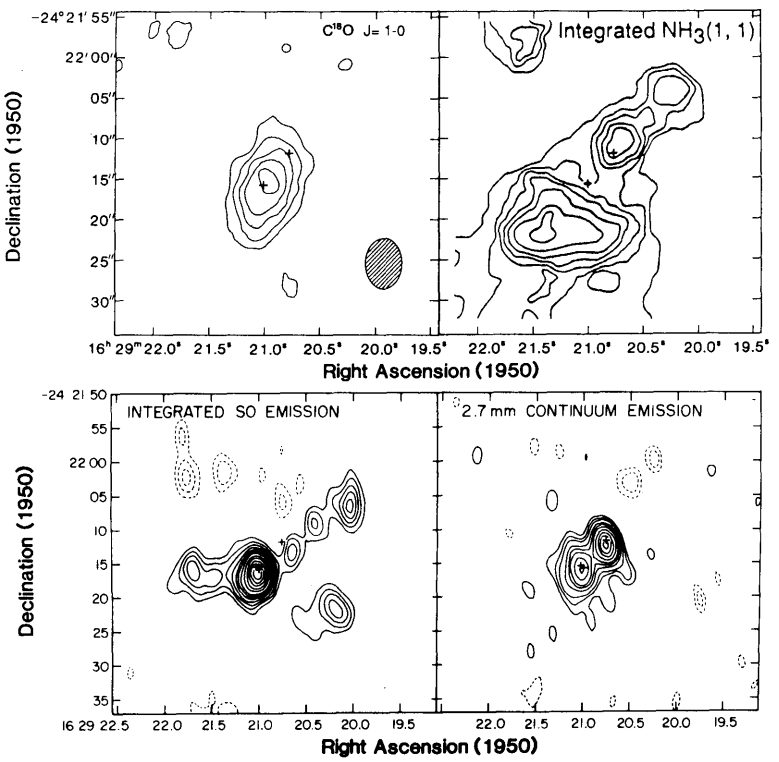

Figure 2. *Composite of emission maps of IRAS 16293 −2422. (a) Velocity integrated $C^{18}O$ J=1→0 map obtained with the Owens Valley Interferometer (OVRO); (b) NH_3 (1,1) map obtained with the VLA; (c) and (d) Integrated SO 2_3–1_2 and 2.7 mm continuum emission mapped with OVRO. The plusses indicate the positions of the 2 cm radio sources. Note that the continuum emission has broken into two sources separated by 830 AU, but that the SO emission is mainly associated with only one of the two (from Refs. 32, 34).*

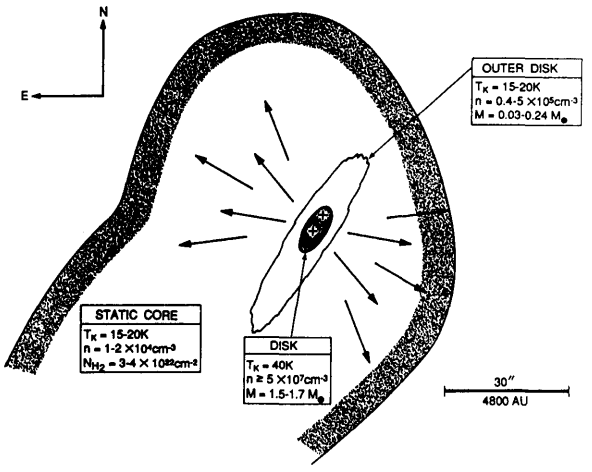

Figure 3. *Graphical depiction of the IRAS 16293 -2422 molecular cloud core and circumstellar disk(s). The long arrows above and below the disk represent the outflow. The hatched outer line approximates the 4.5 K km s^{-1} contour of integrated $C^{18}O$ 1-0 emission (from Ref. 32).*

Single-dish spectra at submillimeter wavelengths cannot spatially resolve such distributions (see Table 1), but can provide valuable information on the overall chemical composition of the region. Fig. 4 demonstrates the quality of data that is now obtainable in only a few minutes of integration time (Ref. 40). Molecules such as HCO^+, HCN, SiO, SO_2, HCS^+ and CH_3OH are readily detected, and in many cases more than one line is visible. For SO_2 and CH_3OH, this leads to rotation diagram temperatures of about 80 K, considerably warmer than the dust.

What processes can give rise to the different molecular distributions and their relative abundances? The energetic outflows and heating due to radiation from newly-formed stars result in the enhancement of selected molecular species. Key molecules generally thought to be associated with these energetic phenomena are HCO^+, SO, SO_2 and SiO (Refs. 38, 39), all of which are prominent in IRAS 16293 -2422. For SO and SO_2, the underlying cause of their small abundances in cold clouds appears to be the depletion of the gas phase sulfur reservoir on grains, as most of the reactions invoked have little temperature dependence. Silicon monoxide is suspected to have at least moderate activation barriers which affect its formation, but it too suffers from severe gas-phase depletion of silicon in cold clouds. The association of SO emission with the SE source (the position where H_2O masers are found) and the distribution of lesser emission E-W along the outflow axis may be an indication that the enhanced SO abundance in IRAS 16293 -2422 is an interaction product of the surrounding molecular material with the outflow, which probably releases sulfur and oxygen back into the gas phase. The shocks associated with the outflow may also result in relatively large abundances of H_2O and OH with which the atomic sulfur and silicon can react to form molecules. HCO^+ appears enhanced as well by the outflow, possibly because of reactions of ionized carbon with OH and H_2O. Since no high-resolution images are yet available for other species such as SiO and SO_2, it is not clear whether their emission is also associated with the outflow, or whether it arises in the warm part of the disk, or results from accretion shocks at the disk boundary.

The $C^{18}O$ and CS molecules are located principally in the disk, and their abundances appear little affected by the outflow. The disparity in relative distributions of $C^{18}O$ and NH_3 may shed some light on the nature of the grain surface chemistry. It is clear that gas-phase NH_3 is down by at least an order of magnitude in the inner core, suggesting that it is depleted onto grains. This behavior is also seen in ammonia relative to CS and dust in the more massive NGC 2071 IRS1 region (Ref. 41).

The question is whether the NH_3 surrounding IRAS 16293 -2422 is remnant interstellar cloud material, or whether it has been depleted and/or formed on grains in the inner part and subsequently returned back to the gas phase. It is interesting to note that both NH_2D and CH_3OH have been detected in IRAS 16293 -2422, molecules which are thought to result from grain surface processes (see below). Water is predicted to have the largest abundance and excitation contrast between the protostellar source and the surrounding cloud, but is presently unobservable even at airborne altitudes. Observation of the highly-excited far-infrared lines of H_2O using *ISO*, and of the lower-lying lines using future space-borne submillimeter missions such as *FIRST* or *SMMM* will be very important. The HDO abundances may exhibit similar characteristics, so that further searches for this species in star-forming regions using ground-based techniques will be very valuable.

Of particular chemical interest is also the detection of extremely high velocity molecular flows associated with young stellar objects (Refs. 42-45). Although such flows have not yet been seen in IRAS 16293 -2422, CO with velocities extending up to 160 km s^{-1} from line center have been found for HH 7-11. The major question is whether the CO is formed in the jet itself, or whether it is ambient material which has recently been swept up by the jet. The latter alternative appears supported by high spatial resolution data (Ref. 44). The high-velocity CO is found to be highly localized and coincides with strong HCO^+ and shocked H_2 emission. The main difficulty with this model is that the CO is unlikely to survive such a powerful shock. Searches for atomic carbon should indicate whether the CO is indeed dissociated further downstream.

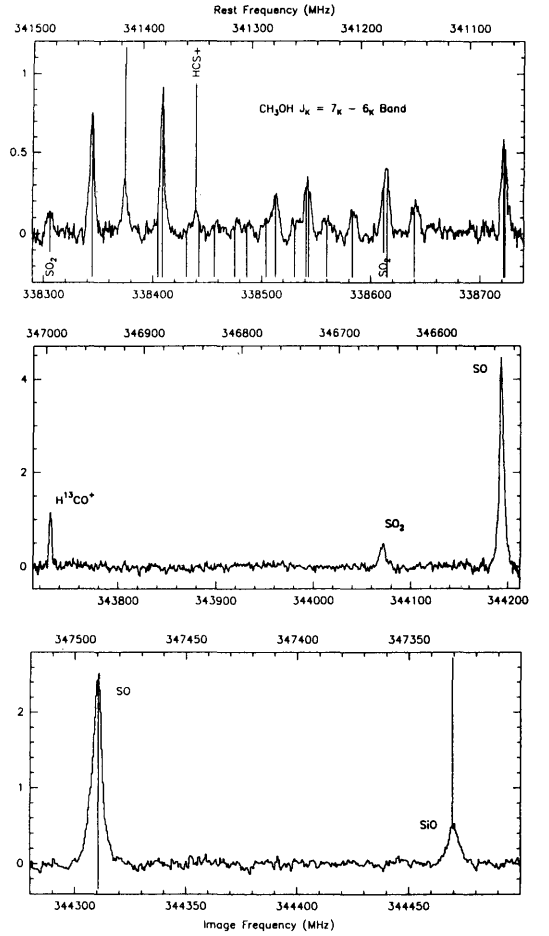

Figure 4. *Submillimeter spectra of IRAS 16293 -2422 obtained with the Caltech Submillimeter Observatory. All spectra give T_A^* (in K) and are double sideband, with the frequency ranges observed labelled on the top and bottom axes (from Ref. 40).*

4.2 High mass star formation: Orion/KL

The Orion/KL region, which includes the luminous infrared sources BN and IRc2, is perhaps the most widely known and best studied example of a young stellar nebula in which high mass star formation occurs. Indeed, because of its proximity, large intrinsic luminosity ($2\text{–}10\times10^4$ $L_\odot$), and enormous quantity of surrounding material, the IRc2 region is one of the brightest compact objects in the sky from mid-infrared to millimeter wavelengths. Its unique strength in molecular line emission has made it not only an irresistible source for molecular line surveys, but has also led to millimeter interferometer maps of many different molecules (Ref. 38).

In single dish spectra with 30–60″ beams centered on Orion/KL, at least 4 different components can be distinguished kinematically: the extended ridge, consisting of quiescent surrounding cloud material; the plateau source, containing shocked material from the interaction of the outflow from IRc2 with the cloud; the compact ridge, a compressed clump of cloud material 10–15″ S of IRc2; and the hot core component, centered on IRc2. These regions are illustrated graphically in Fig. 5. Interferometer maps show that chemical heterogeneity exists in these components on scales of 2000 AU or less. Molecules such as SO, SO_2, SiO and HCO^+ appear mostly associated with the plateau source, much the same as in the case of IRAS 16293 – 2422. We focuss here on the chemistry in the hot core region, which may most resemble that expected in the warm inner part of a disk.

The hot core has a size of about 0.02 pc, temperatures of 100–200 K and densities $n_H \approx 10^7 - 10^9$ cm^{-3}. Because of the high temperatures and densities, the effectiveness of the ion-molecule reactions is reduced. As a result, the abundances of complex carbon-bearing molecules are significantly reduced compared with e.g. the extended ridge. Because the heating is caused by radiation rather than by shocks, grain vaporization does not occur, so that the abundances of the refractory sulfur and silicon species are low, in contrast with the plateau source. On the other hand, the elevated temperatures are sufficient to release much of the grain mantle material stored over the cloud lifetime. Indeed, the composition of the hot core appears consistent with a chemistry that was dominated by ion-molecule reactions in a cold, quiescent dense cloud with accretion onto grains, followed by evaporation of the molecules from the grains once star formation has occurred (Ref. 46). Support for this theory comes from the large observed abundances of deuterated molecules like HDO (Ref. 47), NH_2D (Ref. 48), CH_3OD (Ref. 49) and DCN (Ref. 64), which indicate that significant fractionation is retained even though the kinetic temperature is well above 100 K. The most likely explanation is that the observed deuterated molecules are "fossil" water, ammonia or methanol trapped onto grains, and released only recently when star formation has raised the local temperatures sufficiently to evaporate their icy grain mantles (Refs. 50, 51). If IRc2 is responsible for this heating, it cannot have existed for more than about 10^4 yrs, because otherwise the deuterium enhancements would have been reset by chemical reactions to their high-temperature values. Recall that significant amounts of NH_2D and CH_3OH have also been observed in IRAS 16293 –2422 (§4.1). Grain chemistry may also be responsible for the enhanced abundance of H_2CO, and for the conversion of unsaturated carbon-chain molecules into more hydrogenated species like ethyl cyanide, because the relevant gas phase routes are highly endothermic.

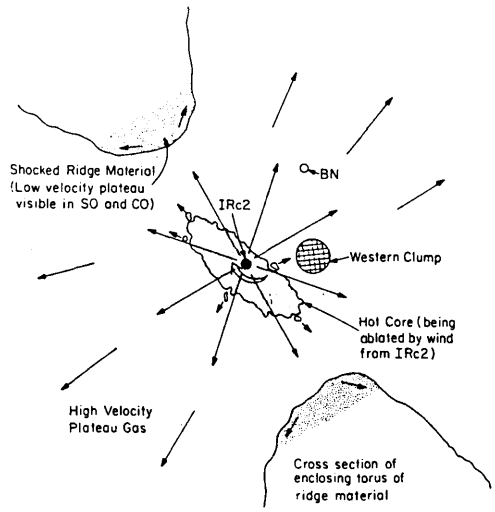

Figure 5. *Schematic model for the Orion/KL outflow region around IRc2. The hot core material (shaded region) lies mainly in front of IRc2, and is being ablated by a wind from IRc2. The resulting material forms the high-velocity plateau. The volume around IRc2 has been largely cleared of material except where the outflow has been stopped by the dense ridge gas. The resulting region (dotted) is responsible for the low-velocity plateau (from Ref. 63).*

Because the hot core is one of the best chemically characterized sources, it is instructive to summarize the observed gas-phase and grain-surface abundances for this case. Orion has several observational advantages over other regions. First, it is warm so that higher-lying lines of molecules like H_2O become observable. Second, at least two bright embedded infrared sources, BN and IRc2, are available against which absorption line observations of dust features and non-polar gas-phase molecules can be performed.

The results are summarized in Table 2. CO is seen to be the most abundant gas-phase molecule by far, with $CO/H_2 \approx 1.2\times10^{-4}$, accounting for about 15% of the carbon. The amount of gas-phase C is uncertain, but is unlikely to be more than 10% of that of CO. Limits on the CH_4 abundance of $CH_4/CO<0.01$ have

TABLE 1. ANGULAR SIZES OF PROTOSTELLAR OBJECTS AND CAPABILITIES OF TELESCOPES

Linear size	Angular size			Telescope	Angular resolution			
	Taurus 140 pc	Orion 450 pc	M17 2.2 kpc		115 GHz	230 GHz	345 GHz	810 GHz
5 AU ..... Inner solar nebula	0.04″	0.01″	...	45 m (Nobeyama)	15″	...	...	...
100 AU ..... Outer solar nebula	0.7″	0.2″	0.05″	30 m (IRAM)	22″	12″	7″	...
1000 AU ..... Protostellar nebula/disk	7″	2″	0.5″	15 m (JCMT/SEST)	44″	22″	15″	6″
0.05 pc ..... Cloud core	74″	23″	5″	10 m (CSO)	...	30″	20″	9″
0.5 pc ..... Cloud	12′	4′	50″	Interferometer (OVRO/BIMA/ Nobeyama)	4–7″	1–2″	...	...

Note: the table only list the capabilities of currently operating telescopes, not those of future projects.

TABLE 2. OBSERVED ABUNDANCES X/H_2 IN ORION

	Species	Hot Core	Ext. Ridge/BN	Other Clouds	Abundance
Gas phase:	CO	1(-4)	5(-5)	(0.5–2)(-4)	15–40% of C; few % of O
	C	...	3(-6)	1(-5)	few % of C
	CH_4	<1(-6)	<1(-6)	<(0.1–1)(-6)	negligible
	C_2H_2	1(-7)	...	1(-7)	negligible
	H_2O	1(-5)	$\lesssim$1(-6)	$\lesssim$1(-5)	few % of O
	O_2	<1(-4)	...	<(1–5)(-5)	<few % of O
	O	<1(-4)	<1(-4)	...	?
	CO_2	...	<1(-6)	<1(-6)	?
	H_2CO	3(-8)	3(-8)	(2–10)(-8)	negligible
	N_2	...	...	1(-5)	dominant?
	NH_3	1(-7)	2(-7)	(0.2–1)(-7)	<1% of N
	N	...	...	...	?
Solid phase:	H_2O	...	3(-5)	(0–1)(-4)	up to 6 % of O
	CO	...	<3(-7)	(0–1)(-5)	up to 1 % of C; 0.5 % of O
	CO_2	...	...	(0–3)(-6)	up to 0.3 % of C, O
	NH_3	...	...	<1(-5)	less than 5 % of N

been obtained from millimeter CH_3D searches (Ref. 38), and from failures to detect the infrared absorption lines of CH_4 toward BN (Ref. 52). C_2H_2 has recently been discovered toward IRc2 with an abundance $C_2H_2/CO \approx 10^{-3}$ (Ref. 53). Thus, neither methane nor acetylene are significant, and more than 80% of the carbon is probably locked up in grains. As much as 50% of this carbon may be in refractory dust components, whereas the remaining 30% is probably in the more volatile mantles. The abundance of solid CO itself is small, however (e.g. Ref. 54).

The oxygen budget in the cloud is much more uncertain. H_2O and its isotopic species have been observed directly in Orion using a variety of observational techniques (Refs. 55–57, 38, 47). All of them indicate that the gas-phase H_2O abundance in Orion/KL is significantly less than that of CO, and accounts for at most a few percent of the total oxygen budget. Indirect limits on the gas-phase O_2 abundance based on searches for lines of $^{16}O^{18}O$ give $O_2/CO<1$ (Ref. 38), so that at most a few % of the oxygen can be locked up in O_2. Atomic oxygen can be measured by its fine-structure transitions at 63 and 145 μm from airborne platforms, but observations indicate $O/CO<1$. Gas-phase CO itself takes up less than 10% of the available oxygen. CO_2 could conceivably be important, but cannot be observed directly. The protonated version $HOCO^+$ has not been detected in Orion, but the lack of molecular ions in general in the hot core makes this limit not very meaningful. In other molecular clouds, $CO_2/CO<0.01$ (Ref. 58). How much oxygen is found on grains? The observed optical depths of the H_2O absorption bands toward BN indicate H_2O (ice)/CO (gas)$\approx$0.5, so that only about 4% of the oxygen is tied up in water ice. Still, the abundance of solid H_2O is more than that of gas-phase H_2O. Silicates may lock up 15–20% of the oxygen. Solid CO_2 has been detected toward other sources with CO_2 (solid) $\approx$ CO (solid) (Ref. 8), but has not yet been found toward IRc2 or BN. In summary, at most 25% of the oxygen in the hot core is detected in gas-phase species, and another 25% may be locked up in known species in grains. This leaves nearly 50% of the oxygen budget unaccounted for.

Most of the nitrogen is thought to reside in the form of N_2, but no estimates have been possible from N_2H^+ due to the lack of ions in the hot core. The NH_3 abundance is about 10^{-7} (Ref. 47), although higher values have been argued. Atomic nitrogen could be significant, but no reliable determinations of its abundance have been made. The amount of nitrogen on grains is unknown, but is unlikely to be in the form of ammonia, since NH_3 (solid)/H_2O (solid)<0.01 has been estimated (Ref. 59).

It is concluded that in spite of the fact that Orion/KL is one of the best studied sources in the sky, major uncertainties remain in the principal oxygen and nitrogen reservoirs in this cloud.

5. CHEMICAL STATE OF PROTOSTELLAR NEBULAE

As the gasses and grains processed in the star-forming region fall into the protostellar nebula, they undergo further chemical and physical transformations before incorporation into solid bodies (Refs. 60, 1). The prevailing view is that interstellar material falls onto an accreting disk and passes through a shock front, where the densities increase from 10^4–10^6 cm^{-3} in the precursor cloud to 10^8–10^{13} cm^{-3} in the disk. In the inner regions, the temperatures are high (>1000 K) and all the dust is evaporated. As the disk cools, the atoms and molecules are thought to condense in a sequence according to their chemical potential, local vapor pressure and ambient temperature; with their abundances governed by thermodynamic equilibrium. Other energetic processes which may affect the chemistry include drag-heating on grains and lightning. In the outer part, however, the chemistry is thought to resemble that of the interstellar cloud from which the disk formed (i.e., kinetically controlled), except in the subnebular regions immediately surrounding accreting proto-Jovian planets. The distance at which the transition from LTE to "interstellar chemistry" occurs is quite uncertain and depends on the amount of turbulent mixing in the nebula.

Our own solar system is currently the only region in which this scenario can be tested, albeit only with relicts available for study. Because comets are generally thought to have undergone the least processing, they may be the most valuable link between the solar nebula and interstellar chemistry. In recent years, a great amount of information has become available on molecular abundances in comets in general, and comet Halley in particular. Still, comparison with interstellar abundances is hampered by the fact that only few parent molecules are observed directly. An enormous step forward in this area would be the *CRAF* and *Rosetta* missions.

Table 3 is a current summary of the abundances for comet Halley (Refs. 61, 62, 1), compared with the interstellar gas-phase and grain-surface abundances. Significant controversy surrounds the amount of CH_4 in comet Halley. The fairest conclusion to be drawn from the data is that comet Halley contains an amalgam of material, some of which was produced in the molecular cloud and not touched again (e.g. HCN, H_2CO?), and some of which represents the chemical evolution in the solar nebula and perhaps giant planet subnebulae (e.g. CH_4?).

TABLE 3. Comparison of Abundances in Comet Halley with Interstellar Clouds

Species	Halley	ISM (gas)[a]	ISM (grains)[a]
H_2O	1	1	1
CO	0.05-0.1	10	0-0.13
N_2	<0.05	10:	...
CH_4	0.05?	<0.1	<0.01
NH_3	0.003-0.01	0.01	<0.1
CO_2	0.02-0.04	<0.1	0-0.03
H_2CO	0.01-0.1	0.002	...
HCN	0.001	0.03	...

[a] The interstellar values refer mostly to the Orion hot core.

6. CONCLUSIONS

It is evident from the preceeding sections that many different processes can modify the chemical composition of a cloud as it evolves from its initial quiescent state to the protostellar regime. The examples of IRAS 16293 -2422 and Orion/KL demonstrate that the star formation process modifies the chemistry in at least two ways: by changing molecular depletions and by creating energetic events. The observed high abundances of deuterated molecules in the hot core in Orion/KL and other massive star forming regions form perhaps the best evidence that molecular mantles are released from grains when heated to temperatures in excess of 100 K. The distribution of NH_3 in IRAS 16293 -2422 may be the first case study of the depletion of molecules in the inner core, and return to the gas phase in the outer part. The extent to which grains actively form new molecules, rather than just being a sink of them, is still an open question, however, and the actual chemistry of NH_3 is still poorly understood both in the gas phase and on cryogenic, disordered surfaces.

The two most obvious signposts of energetic phenomena associated with star formation are infrared emission from warm dust and large scale molecular outflows. The chemistry naturally responds to these energetic events. Physically, the increased temperature opens up normally closed chemical channels for the destruction and creation of species such as H_2O. If strong enough, the shocks can not only vaporize mantles, but also disrupt grain cores and return sulfur and silicon to the gas phase. The large amounts of SO, SO_2, SiO and HCO^+ observed in star-forming regions most likely result from the interaction of the outflow with the surrounding material, although the details of the chemistry still need to be worked out. The enhancements appear to depend little on the initial mass of the source. Clearly, much of the same chemical processes inferred for the Orion/KL hot core also occur in IRAS 16293 -2422, despite the three decade drop in stellar luminosity.

It is evident that the study of the chemistry in star forming regions is still in its infancy. Significant advances are expected in the coming years through ground-based infrared and (sub)millimeter observations. Future space missions such as *ISO*, *FIRST/SMMM*, *CRAF* and *Rosetta* are anxiously awaited.

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